Polycarbonate and moulded bodies thereof

The present invention relates to a novel polycarbonate and its use as a material for the production of moulded bodies and semi-finished products, especially for transparent applications, such as data stores or audio compact disks, sheets, multi-wall sheets, films, lamp housings, panes, especially panes for motor vehicles, headlamp lenses, but also for electrical applications or house building.

The preparation of aromatic polycarbonates by the melt transesterification process is known from the literature and is described, for example, in the Encyclopedia of Polymer Science, Vol. 10 (1969), Chemistry and Physics of Polycarbonates, Polymer Reviews, H. Schnell, Vol. 9, John Wiley and Sons, Inc. (1964) and, starting from DE 1 031 512, in some patents.

In EP-B-360 578 there are described polycarbonates containing end groups other than phenol. The polycarbonates obtained according to EP 360 578 have a markedly increased content of erroneous structures as compared with the polycarbonates synthesised in solution. As a result, such materials have disadvantages as regards melt stability, thermostability and constancy of colour.

The object was, therefore, to develop polycarbonates and a process for their preparation, having greater stability.

The object has been achieved by the synthesis of polycarbonates having a markedly reduced concentration of erroneous structures.

The present invention provides solvent-free, low-branching, thermoplastic, aromatic polycarbonates prepared by the transesterification process and having weight-average molecular weights M_w of from 2000 to 150,000, preferably from 4500 to 55,000, based on diphenols, chain terminators of formula (I)

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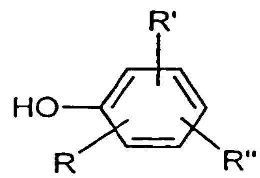


(I)

wherein R, R' and R" may each independently of the others represent H, optionally branched C_1-C_{34}-alkyl/cycloalkyl, C_7-C_{34}-alkaryl or C_6-C_{34}-aryl, and, optionally, branching agents, characterised in that structural elements of formula (II)

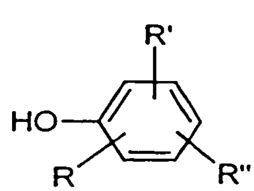
$$\text{HO-Z(COOH)-OH} \qquad \text{(II)}$$

have a value after total saponification and HPLC determination of less than 300 ppm, preferably from 0.03 ppm to 250 ppm, Z being as defined for formula (VI) and the acid group being in the ortho position relative to a hydroxy group.

As compared with polycarbonates mis-structured in the usual manner, the polycarbonates according to the invention exhibit a substantially increased hydrolytic stability and an improved critical thickness, with otherwise comparable mechanical and thermal properties.

The polycarbonates according to the invention are prepared in the melt from dihydroxy compounds, dicarbonates, chain terminators and, optionally, branching agents.

Chain terminators within the context of the invention are those of formula (I)

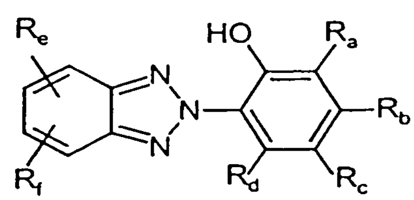


(I)

wherein R, R' and R" may each independently of the others represent H, optionally branched C_1-C_{34}-alkyl/cycloalkyl, C_7-C_{34}-alkaryl or C_6-C_{34}-aryl, for example

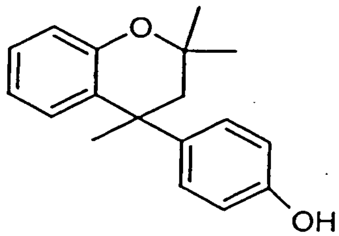
o-n-butylphenol, m-n-butylphenol, p-n-butylphenol,
o-isobutylphenol, m-isobutylphenol, p-isobutylphenol,
o-tert-butylphenol, m-tert-butylphenol, p-tert-butylphenol,
o-n-pentylphenol, m-n-pentylphenol, p-n-pentylphenol,
o-n-hexylphenol, m-n-hexylphenol, p-n-hexylphenol,
o-cyclohexylphenol, m-cyclohexylphenol, p-cyclohexylphenol,
o-phenylphenol, m-phenylphenol, p-phenylphenol,
o-isooctylphenol, m-isooctylphenol, p-isooctylphenol,
o-n-nonylphenol, m-n-nonylphenol, p-n-nonylphenol,
o-cumylphenol, m-cumylphenol, p-cumylphenol,
o-naphthylphenol, m-naphthylphenol, p-naphthylphenol,
2,5-di-tert-butylphenol, 2,4-di-tert-butylphenol, 3,5-di-tert-butylphenol,
2,5-dicumylphenol, 3,5-dicumylphenol,
4-phenoxyphenol, 2-phenoxyphenol, 3-phenoxyphenol,
3-pentadecylphenol, 2-pentadecylphenol, 4-pentadecylphenol,
2-phenylphenol, 3-phenylphenol, 4-phenylphenol,
tritylphenol, 3-triphenylmethylphenol, 2-triphenylmethylphenol,

also benzotriazole derivatives of the general formula (III)

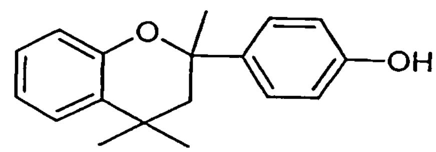


(III)

wherein R_a to R_f are as defined above for R, R' and R",
and chroman compounds such as

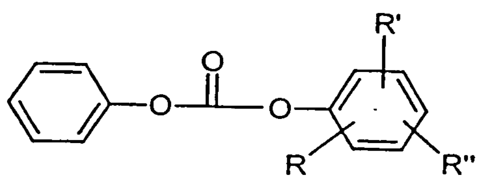


and



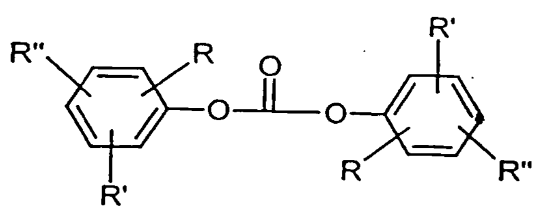
preferably high-boiling phenols such as tritylphenol, cumylphenol, pentadecylphenol or chromans,

or also in the form of compounds that are capable of transesterification under the synthesis conditions, such as, for example, carbonates, oxalates, o-carboxylic acid esters or the like, with preference being given to the free phenols or the carbonic acid diesters of formula (IV)



(IV)

and formula (V)



(V)

wherein R, R' and R" correspond to those of formula (I). Phenols or transesterification-active substances can be added to the synthesis individually or in the form of a mixture. Preferred mixtures are those with diphenyl carbonate. It is possible to add the phenol or the phenol-carrying compound at any time during the reaction, preferably at the beginning of the reaction, and the addition can be divided

into several portions. The total amount of carbonic acid ester is from 100 to 130 mol%, preferably from 103 to 120 mol%, based on the dihydroxy compound.

For the preparation of polycarbonates by the process according to the invention it is possible to use a chain terminator or a mixture of several chain terminators, so that there may be present as an end group in the polycarbonate according to the invention phenol but also phenol together with other chain terminators. From 0.4 to 17 mol%, particularly preferably from 1.3 to 8.6 mol% (based on the dihydroxy compound), of chain terminator are preferably added. The addition may take place either before the reaction or wholly or partially during the reaction.

Dihydroxy compounds within the context of the invention are those of formula (VI)

$$\text{HO-Z-OH} \qquad \text{(VI)}$$

in which Z is an aromatic radical having from 6 to 30 carbon atoms which may contain one or more aromatic nuclei, may be substituted and may contain aliphatic or cycloaliphatic radicals or alkylaryls or hetero atoms as bridge members.

Examples of dihydroxy compounds of formula (VI) are
hydroquinone,
resorcinol,
dihydroxydiphenyls,
bis-(hydroxyphenyl)-alkanes,
bis-(hydroxyphenyl)-cycloalkanes,
bis-(hydroxyphenyl) sulfides,
bis-(hydroxyphenyl) ethers,
bis-(hydroxyphenyl) ketones,
bis-(hydroxyphenyl)-sulfones,
bis-(hydroxyphenyl) sulfoxides,

α,α'-bis-(hydroxyphenyl)-diisopropylbenzenes
and their nuclear-alkylated and nuclear-hydrogenated compounds.

These and other suitable diphenols are described, for example, in US-A 3 028 365, 3 148 172, 3 275 601, 2 991 273, 3 271 367, 3 062 781, 2 970 131 and 2 999 846, in German Offenlegungsschrift 1 570 703, 2 063 050, 2 063 052, 2 211 0956, in French Patent Specification 1 561 518 and in the monograph "H. Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York 1964".

Examples of preferred diphenols are:
4,4'-dihydroxydiphenyl,
2,2-bis-(4-hydroxyphenyl)propane,
2,4-bis-(4-hydroxyphenyl)-2-methylbutane,
1,1-bis-(4-hydroxyphenyl)cyclohexane,
1,1-bis-(4-hydroxyphenyl)-4-methylcyclohexane,
α,α'-bis-(4-hydroxyphenyl)-p-diisopropylbenzene,
α,α'-bis-(4-hydroxyphenyl)-m-diisopropylbenzene,
bis-(4-hydroxyphenyl)sulfone,
bis-(4-hydroxyphenyl)methane,
1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane,
2,2-bis-(2,6-dimethyl-4-hydroxyphenyl)propane,
2,2-bis-(4-hydroxyphenyl)hexafluoropropane,
1,1-(4-hydroxyphenyl)-1-phenylethane,
bis-(4-hydroxyphenyl)diphenylmethane,
dihydroxydiphenyl ether,
4,4'-thiobisphenol,
1,1-bis-(4-hydroxyphenyl)-1-(1-naphthyl)ethane,
1,1-bis-(4-hydroxyphenyl)-1-(2-naphthyl)ethane,
2,3-dihydroxy-3-(4-hydroxyphenyl)-1,1,3-trimethyl-1*H*-inden-5-ol,
2,3-dihydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethyl-1*H*-inden-5-ol,

2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1*H*-indene]-5,5'-diol.

Special preference is given to
resorcinol,
1,1-bis-(4-hydroxyphenyl)-1-(1-naphthyl)ethane,
1,1-bis-(4-hydroxyphenyl)-1-(2-naphthyl)ethane,
2,2-bis-(4-hydroxyphenyl)propane,
α,α'-bis-(4-hydroxyphenyl)-p-diisopropylbenzene,
α,α'-bis-(4-hydroxyphenyl)-m-diisopropylbenzene,
1,1-bis-(4-hydroxyphenyl)cyclohexane,
1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane,
bis-(4-hydroxyphenyl)diphenylmethane,
4,4'-dihydroxydiphenyl.

It is possible to use both one diphenol of formula (VI), with formation of homopolycarbonates, and several diphenols of formula (VI), with formation of copolycarbonates.

Low-branching within the context of the invention means that the content of formula (II) in the polycarbonate has a value after total saponification and HPLC determination of less than 300 ppm, preferably from 0.03 ppm to 250 ppm.

The polycarbonates can be branched in a deliberate and controlled manner by the use of small amounts of from 0.02 to 3.6 mol% (based on the dihydroxy compound) of branching agents. Suitable branching agents are the compounds which are suitable for the preparation of polycarbonates and contain three or more functional groups, preferably those containing three or more than three phenolic OH groups.

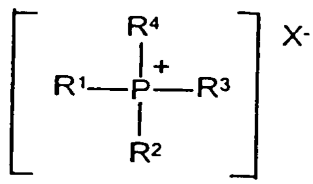
Examples of suitable branching agents are
phloroglucinol,

4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)heptane,
1,3,5-tri-(4-hydroxyphenyl)benzene,
1,1,1-tri-(4-hydroxyphenyl)ethane,
tri-(4-hydroxyphenyl)phenylmethane,
2,2-bis-[4,4-bis(4-hydroxyphenyl)cyclohexyl]propane,
2,4-bis-(4-hydroxyphenyl-isopropyl)phenol,
2,6-bis-(2-hydroxy-5-methylbenzyl)-4-methylphenol,
2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)propane,
hexa-[4-(4-hydroxyphenyl-isopropyl)phenyl]orthoterephthalic acid ester,
tetra-(4-hydroxyphenyl)methane,
tetra-[4-(4-hydroxyphenyl-isopropyl)phenoxy]methane,
1,4-bis-[4',4"-dihydroxytriphenyl)methyl]benzene,
α,α',α"-tris-(4-hydroxyphenyl)-1,3,4-triisopropenylbenzene,
isatinbiscresol,
pentaerythritol,
2,4-dihydroxybenzoic acid,
trimesic acid,
cyanuric acid.

1,1,1-tri-(4-hydroxyphenyl)ethane and isatinbiscresol are particularly preferred.

As catalyst for the preparation of the polycarbonates according to the invention there may be used phosphonium salts, optionally in combination with other suitable catalysts which do not lead to erroneous structures such as formula (II), such as, for example, other onium compounds.

Phosphonium salts within the context of the invention are those of formula (VII)



(VII)

wherein R^{1-4} may be the same or different C_1-C_{18}-alkyls, C_6-C_{14}-aryls, C_7-C_{12}-aralkyls or C_5-C_6-cycloalkyls, preferably methyl or C_6-C_{14}-aryls, particularly preferably methyl or phenyl, and X^- may be an anion, such as a sulfate, hydrogen sulfate, hydrogen carbonate, carbonate, acetate, boranate, hydrogen phosphates, a halide, preferably a fluoride, chloride or bromide, or an alcoholate of the formula OR wherein R may be C_6-C_{14}-aryl or C_7-C_{12}-aralkyl, preferably phenyl.

Preferred catalysts are
tetraphenylphosphonium fluoride,
tetraphenylphosphonium tetraphenylboranate,
particularly preferably tetraphenylphosphonium phenolate.

The preparation of the polycarbonates according to the invention is carried out, for example, as follows: in the first step, the diphenols, the carbonic acid diesters, the catalyst and, optionally, the alkylphenols and branching agents are melted at temperatures of from 75°C to 225°C, preferably from 105°C to 235°C, particularly preferably from 120°C to 190°C, under normal pressure within a period of from 0.1 to 5 hours, preferably from 0.25 to 3 hours. Then the oligocarbonate is prepared by applying a vacuum and raising the temperature by removing the monophenol by distillation. In the last step, the polycarbonate is prepared in the polycondensation by raising the temperature further to from 240°C to 325°C and at a pressure of < 2 mbar.

In the preparation of polycarbonates by the melt transesterification process, the reaction of the bisphenol and the carbonic acid diester may be carried out

continuously or discontinuously, for example, in stirrer vessels, thin-layer evaporators, falling film evaporators, stirrer vessel cascades, extruders, kneaders, simple disk reactors and high-viscosity disk reactors.

Isolation of the polycarbonates according to the invention is likewise carried out in a known manner, for example by removing, spinning and granulating.

The polycarbonates according to the invention can have weight-average molecular weights M_w of approximately from 2000 to 150,000, preferably approximately from 4500 to 55,000, M_w being determined *via* the relative solution viscosity in dichloromethane or in mixtures of equal amounts by weight of phenol/o-dichlorobenzene, calibration being by means of light scattering.

The polycarbonates according to the invention have the usual OH end group contents known from the literature, which can be determined by photometry using titanium tetrachloride.

The polycarbonates according to the invention can be processed thermoplastically in the usual manner at temperatures of from 260°C to 320°C. Moulded bodies and films of any kind can be produced in a known manner by injection moulding or by means of extrusion.

The polycarbonates according to the invention are readily soluble in solvents such as chlorinated hydrocarbons, for example methylene chloride, and can therefore be processed, for example, in a known manner to cast films.

Accordingly, the invention also provides a process for the preparation of the low-branching polycarbonates according to the invention, characterised in that there are used as catalyst phosphonium salts of formula (VII) in concentrations of from 10^{-2} mol to 10^{-6} mol, based on 1 mol of diphenol, optionally in combination with

other suitable catalysts which do not lead to erroneous structures such as formula (II), such as, for example, other onium compounds.

In order to improve the properties, auxiliary substances and reinforcing agents can be added to the polycarbonates according to the invention. The following, *inter alia*, are to be taken into consideration as such: stabilisers, flow auxiliaries, mould-release agents, fireproofing agents, pigments, finely divided minerals, fibrous materials, for example alkyl and aryl phosphites, phosphates and phosphanes, low-molecular-weight carboxylic acid esters, halogen compounds, salts, chalk, quartz powder, glass and carbon fibres, pigments and combinations thereof.

Other polymers, for example polyolefins, polyurethanes, polyesters and polystyrene, may also be added to the polycarbonates according to the invention.

Excellent properties are achieved with that material even in moulded bodies.

Accordingly, the present invention relates also to the use of the low-branching, solvent-free, aromatic polycarbonates according to the invention for the production of moulded bodies and semi-finished products, especially for transparent applications, such as data stores or audio compact disks, sheets, multi-wall sheets, films, lamp housings, panes, especially panes for motor vehicles, headlamp lenses, but also for electrical applications or house building.

Examples

Comparison Example 1

45.60 g (0.2 mol) of bisphenol A, 47.08 g (110 mol%, based on bisphenol A) of diphenyl carbonate, 3.7 mg (0.03 mol%, based on bisphenol A) of boric acid and 2.12 g (5 mol%, based on bisphenol A) of 4-cumylphenol are weighed into a 500 ml three-necked flask equipped with a stirrer, an internal thermometer and a Vigreux column (30 cm, mirrored) with a bridge. The apparatus is freed of atmospheric oxygen by applying a vacuum and flushing with nitrogen (three times) and the mixture is melted at 180°C and stirred for 30 minutes. Then 36.5 mg (0.03 mol%, based on bisphenol A) of a 15% ammonium hydroxide solution and 0.5 mg (0.003 mol%, based on bisphenol A) of sodium hydrogen carbonate are added and stirring is continued for a further 30 minutes. The temperature is raised to 210°C and the vacuum is increased to 200 mbar and the phenol that forms is removed by distillation. After one hour, the temperature is raised to 240°C and after 20 minutes the vacuum is reduced to 150 mbar. After a further 20 minutes, the pressure is lowered to 100 mbar and maintained for 20 minutes. Then the pressure is reduced to 15 mbar for 30 minutes. The temperature is then raised to 270°C, the vacuum is reduced to 0.5 mbar and stirring is carried out for a further 2 hours. The results are summarised in Table 1.

Example 1

As Comparison Example 1, but 4.9 mg (0.004 mol%, based on bisphenol A) of tetraphenylphosphonium phenolate (which is metered in in the form of mixed crystal containing 30 wt.% phenol, based on the mixed crystal) are added instead of tetramethylammonium hydroxide. Sodium hydrogen carbonate and boric acid are not added. The results are summarised in Table 1.

Example 2

45.66 g (0.2 mol) of bisphenol A, 47.13 g (110 mol%, based on bisphenol A) of diphenyl carbonate, 4.9 mg (0.004 mol%, based on bisphenol A) of tetraphenylphosphonium phenolate (which is metered in in the form of mixed crystal containing 30 wt.% phenol, based on the mixed crystal) and 2.12 g (5 mol%, based on bisphenol A) of 4-cumylphenol are weighed into a 500 ml three-necked flask equipped with a stirrer, an internal thermometer and a Vigreux column (30 cm, mirrored) with a bridge. The apparatus is freed of atmospheric oxygen by applying a vacuum and flushing with nitrogen (three times) and the mixture is melted at 150°C. The temperature is raised to 190°C and the vacuum is increased to 100 mbar and the phenol that forms is removed by distillation. After 20 minutes, the temperature is raised to 235°C and the vacuum is reduced to 60 mbar. After 15 minutes, the temperature is raised to 250°C and after a further 15 minutes the vacuum is increased to 5 mbar. The mixture is then heated to 280°C and the pressure is reduced to 0.5 mbar after 15 minutes. After a further 15 minutes, the mixture is stirred at 300°C for a further 30 minutes. The results are summarised in Table 1.

Example 3

45.66 g (0.2 mol) of bisphenol A, 47.13 g (110 mol%, based on bisphenol A) of diphenyl carbonate, 4.9 mg (0.004 mol%, based on bisphenol A) of tetraphenylphosphonium phenolate (which is metered in in the form of mixed crystal containing 30 wt.% phenol, based on the mixed crystal) and 3.05 g (5 mol%, based on bisphenol A) of 3-pentadecylphenol are weighed into a 500 ml three-necked flask equipped with a stirrer, an internal thermometer and a Vigreux column (30 cm, mirrored) with a bridge. The apparatus is freed of atmospheric oxygen by applying a vacuum and flushing with nitrogen (three times) and the mixture is melted at 150°C. The temperature is raised to 190°C and the vacuum is increased to 100 mbar and the phenol that forms is removed by distillation. After 30 minutes, the temperature is

raised to 235°C, and after a further 30 minutes it is increased to 300°C. The vacuum is slowly reduced to 0.5 mbar and the mixture is stirred for a further 30 minutes. The results are summarised in Table 1.

Example 4

1141.47 g (5 mol) of bisphenol A, 1113.94 g (104 mol%, based on bisphenol A) of diphenyl carbonate and 122.5 mg (0.004 mol%, based on bisphenol A) of tetraphenylphosphonium phenolate (which is metered in in the form of mixed crystal containing 30 wt.% phenol, based on the mixed crystal) are weighed into a stirred container. The container is freed of atmospheric oxygen by applying a vacuum and flushing with nitrogen (three times) and the mixture is melted at 150°C. The temperature is raised to 190°C and the vacuum is increased to 100 mbar and the phenol that forms is removed by distillation. After 60 minutes, the temperature is raised to 235°C, and after a further 30 minutes the vacuum is slowly reduced to 60 mbar and stirring is carried out for a further 15 minutes. The mixture is then heated to 250°C and after 15 minutes the pressure is lowered to 5 mbar for a short time. The results are summarised in Table 1.

Table 1

	Chain terminator	Formula (II) [ppm]	Solution viscosity
Comparison Example 1	cumylphenol/phenol	303	1.142
Example 1	cumylphenol/phenol	70	1.160
Example 2	cumylphenol/phenol	25	1.122
Example 3	pentadecylphenol/phenol	86	1.161
Example 4	phenol	12	1.124